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14. ABSTRACT
The main focus of this project is the study of Gadolinium doped Gallium Nitride. Calculations were carried out to elucidate the origin of the reported above room temperature ferro-magnetism in this system and the occurrence of much larger magnetic moments per Gd than the nominal moment of a Gd3+ ion. Defects are now thought to be responsible for the magnetism. While others proposed Ga vacancies were responsible, the present work showed that Ga vacancies in the triple negative charge state, which is the most likely charge state in semi-insulating samples,

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Report Title

Final Report on Rare-earth doping and co-doping of GaN for magnetic and luminescent applications

ABSTRACT

The main focus of this project is the study of Gadolinium doped Gallium Nitride. Calculations were carried out to elucidate the origin of the reported above room temperature ferro-magnetism in this system and the occurrence of much larger magnetic moments per Gd than the nominal moment of a Gd3+ ion. Defects are now thought to be responsible for the magnetism. While others proposed Ga vacancies were responsible, the present work showed that Ga vacancies in the triple negative charge state, which is the most likely charge state in semi-insulating samples, would not carry a magnetic moment. The neutral charge state held responsible for the magnetism by others was pointed out to be a very high energy of formation defect. Instead it is proposed that nitrogen and oxygen interstitials could play a crucial role in the magnetism. They show long-range ferromagnetic interactions, are likely defects caused by the implantation of Gd and/or growth disturbance and are relatively low energy defects. Furthermore, they are attracted toward Gd dopants. A recent proposal in literature about the role of Gd on N sites and pairs of Gd on adjacent Ga and N sites was evaluated and found to be unrealistic because of the hight energy of formation of Gd on N sites.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Interstitial-nitrogen- and oxygen-induced magnetism in Gd doped GaN,
Chandrima Mitra and Walter R. L. Lambrecht, Phys. Rev. B 80, 081202 (R)
(2009)

First-principles calculations of elasticity, polarization-related properties, and nonlinear optical coefficients in Zn-IV-N2 compounds
Tula R. Paudel and Walter R. L. Lambrecht, Phys. Rev. B 79, 245205 (2009)

Computational study of phonon modes in short-period AlN/GaN superlattices
Tula R. Paudel and Walter R. L. Lambrecht
Phys. Rev. B 80, 104202 (2009)

Comparison between experiment and calculated band structures for DyN and SmN
A. R. H. Preston, S. Granville, D. H. Housden, B. Ludbrook, B. J. Ruck, H. J. Trodahl, A. Bittar, G. V. M. Williams, J. E. Downes, A. DeMasi, Y. Zhang, K. E. Smith, and W. R. L. Lambrecht
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(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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(c) Presentations

Defect induced ferromagnetism in Gd doped GaN, C. Mitra and W. R. L. Lambrecht, APS March meeting 2009, BAPS.2009.MAR.W22.7

First Principles Calculations for Gd doped GaN. Chandrima Mitra and Walter R.L Lambrecht, MRS Fall Meeting 2008, Symposium D: Rare-Earth Doping of Advanced Materials for Photonic Applications, abstract D3.2

Site dependence of electronic structure of Gd impurities in GaN.
Tawinan Cheiwchanchamnangij, Atchara Punya, and Walter R. L. lambrecht
MRS Fall Meeting 2010, SymposiumI: Magnetism and Correlated Electronic Structure of Nitrides; Rare-Earth and Transition Metals and Constituents and Dopants

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

Walter R. L. Lambrecht, Paul Larson,
Gadolinium and Oxygen co-doping of Gallium Nitride: an LSDA + U study,
in "Advances in III-V Nitride Semiconductor Materials and Devices,"
MRS Proceedings Volume 955E (Electronic Publication Only -- No Book Published), Editors: C.R. Abernathy, H. Jiang, J.M. Zavada, paper no. 0955-I01-05
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Site dependence of electronic structure of Gd impurities in GaN.

Tawinan Cheiwchanchamnangij, Atchara Punya, and Walter R. L. lambrecht
in preparation for MRS Symposium Proceeding,
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Patents Submitted

Patents Awarded

Graduate Students

NAME	PERCENT_SUPPORTED
Chandrima Mitra	1.00
Adisak Boonchun	0.05
Tawinan Cheiwchanchamnangij	0.50
Atchara Punya	0.25
FTE Equivalent:	**1.80**
Total Number:	**4**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Walter R. L. Lambrecht	0.08	No
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FTE Equivalent:	
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Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Chandrima Mitra	
Total Number:	**1**

Names of other research staff

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Final Report

Rare-earth doping and co-doping of GaN for magnetic and luminescent applications

Contents

1 Introduction

The primary goal of this project was to elucidate the origin of ferromagnetism in Gadolinium doped Gallium Nitride. Ferromagnetism persisting above 400 K was first reported for Gd doped GaN by Teraguchi et al. [1, 2]. The system attracted strong interested after Dhar et al.[3] reported the occurrence of "colossal magnetic moments", i.e. magnetic moments per Gd of order 4000 μ_B. This claim was rather controversial and finding a quantitative explanation for this unusual phenomenon is a challenge. While the authors of that paper originally proposed[4] that the magnetic moments arise from polarization of the host semiconductor within "spheres of influence" of order 50 nm, the reason for this unusually strong polarization remained unclear. Subsequent studies by several groups indicated that the origin of this magnetism is defect related.[5, 6] While a few other groups have been able to see signs of magnetism in this system,[7, 8] none reported explicitly the very high magnetic moments, which rely on measuring precisely the very dilute Gd concentrations. It is only in the regime of doping as low as 10^{15} cm^{-3} that colossal magnetic moments were claimed to occur. Evidence for Gd and other rare-earth induced magnetism were found also for Gd-doped AlN,[9] for Eu,[10] Tm [11], Er [12, 13] and related observations were made of luminescence from these rare -earth ions. Hite et al. [7] found an increased magnetic effect with Si-codoping but a quenching of the magnetism by proton irradiation,[8] which was however reversible by annealing. Others [14, 15] found traces of secondary phases, none of which,

however, can quite explain the ferromagnetism above room temperature. Paramagnetic/ferromagnetic resonance studies by Kammermeier et al. [16] found no conclusive signals that could account for the high temperature magnetism although some evidence for either Gd or GdN clusters. The fact that implantation leads to even higher magnetization but annealing reduces it somewhat[5, 6] strongly suggests that defects are responsible. X-ray magnetic circular dichroism (XMCD) studies[17, 18] show that the Gd L_3 edge XMCD signal does not follow the hysteresis observed by SQUID (superconducting quantum interference device) measurements, indicating that the main origin of the magnetism does not arise from Gd itself.

On the theoretical side, the first attempt at an explanation came from Dalpian and Wei [19] who proposed an $s - f$ coupling model, in which the conduction band is spin-split by the interaction with minority spin Gd-f electrons. Subsequently, Larson and Lambrecht ,[20] elaborated on this model, showing that with donor concentrations due to oxygen of order 1000 times larger than the Gd concentration, the colossal moments could possibly be explained if a Gd leads to a sufficiently large spin splitting and donor electrons would be ionized to fill only the minority spin split-off band.

The increasing experimental evidence for a defect origin of the magnetism in Gd-doped GaN, led to the suggestion by Liu et al. [21] that Ga vacancies were responsible. Dev et al. [22] suggested that Ga vacancies on their own without even any Gd can lead to ferromagnetism and exhibit rather strong and long-range couplings between them. The Ga-vacancy model was recently further explored by Gohda and Oshiyama [23] who showed that by adding increasingly more vacancies per Gd, magnetic moments as large as 220 μ_B could be obtained for 71 Ga-vacancies per Gd. None of these works however addressed the question, why such a large number of Ga vacancies would form in the presence of Gd.

The specific goals of the present project and the main results are described in the following sections.

2 Statement of the Problem Studied

The broad goal of the proposal was to investigate the magnetic behavior of rare-earth impurities in semiconductors and their possible role in facilitating dilute magnetic semiconductors. At the same time we anticipated working on luminescent properties of rare-earths in GaN as a secondary topic once the magnetic properties were understood or in support of experimental investigations that use the optical luminescence to obtain information on the

rare-earth behavior in GaN. While other rare-earths besides Gd are also of interest, and in particular are of interest for their luminescent opto-electronic applications, it was decided to focus on the Gd doping induced magnetism in GaN.

The initial goal was to elaborate on the model proposed by Dalpian and Wei [19] following preliminary work in our group by Larson [20]. It soon however became clear that this model was untenable. Essentially, the spin-splitting induced by the $s - f$ coupling was found to be proportional to concentration of Gd and while splittings of the order of 50 meV as required to explain colossal moments were found for concentrations of a few percent, the spin-splitting is then predicted to become negligible for the dilute concentrations where the colossal magnetic moment behavior was claimed to exist.[24]

In view of the prevailing experimental skepticism about Dhar et al.'s results [3], we then decided to focus on the more realistic claims of ferromagnetism rather than the colossal magnetic moment issue. Our initial findings in this context were that Gd in GaN couples antiferromagnetically. This agreed with Dalpian and Wei's results[19] but contrary to their results we found p-type doping rather than n-type doping to change the coupling to being ferromagnetic. Our goal at that time was to figure out the origins of this discrepancy. While this work was on-going, new ideas about defect-origins of the magnetism started surfacing and we re-oriented our work toward studying point defect origins. We critically reviewed the proposed Ga-vacancy model and to found it could also not stand muster. We decided to investigate alternative defect models, such as interstitials. This finally led to a promising new model.

During the course of the project, some sidelines of research were explored. These are described at the end of the following results section.

3 Summary of Most Important Results

The most important result of the project was that none of the previous models proposed in literature for explaining the Gd-doped colossal magnetism and ferromagnetism were viable when critically examined. Instead, we found that nitrogen interstitials as well as oxygen interstitials are likely to play a key role in the magnetism.

First, the Dalpian and Wei [19] conduction band splitting model with the spin-split conduction band being filled by donor electrons was found to be inadequate to explain the dilute limit because the spin-spin splitting

in that limit becomes negligible so that the spin split off part of the band can not hold enough electrons to explain the colossal moments. From our calculations of the induced magnetic moments on neighboring atoms to Gd, we could find no evidence for the polarization of the host atoms as proposed by Dhar et al. [3, 4] either. Even giving up on explaining colossal moments, we found that electron free carrier induced coupling between Gd atoms made them more antiferromagnetic rather than ferromagnetic in contrast to the results published by Dalpian and Wei[19]. It was instead found that p-type doping could possibly make the interactions weakly ferromagnetic. All these results were described primarily at conferences and in Chandrima Mitra's Ph.D. thesis [24] but were not in themselves deemed sufficient to justify a peer reviewed journal article.

The appearance of Liu et al.'s [21] paper proposing Ga vacancies were responsible for the magnetism in this system, led to a change in our research direction. While initially, this seemed a promising idea and in fact consistent with our findings of ferromagnetic coupling for p-type doping, it soon became clear to us that this model also had problems. In fact, inspection of the old literature on point defects in GaN showed right away that Ga vacancies in the neutral charge state, studied by these authors as well as by Dev et al. [22] have the highest energy of formation among all native point defects in GaN. Hence, how can one explain where the Ga vacancies would come from? The older literature on point defects in GaN however did not consider or discuss magnetic properties. We thus initiated calculations of various defects in the presence of Gd in the sample.

We initially followed the idea that strain relieve might be the cause for Ga vacancy formation: Gd substitution on Ga make the lattice expand, while Ga vacancies would make the lattice contract. We estimated this effect quantitatively and found that about 20 Ga vacancies are required per Gd to keep the lattice volume unchanged. However, thinking more about this result, we realized that there is no reason why the lattice constant would not expand by Gd. In fact, samples with Gd do show a lattice expansion. We concluded that the total energies are the more appropriate quantity to examine and this would preclude the formation of Ga vacancies. Furthermore, we realized that for semi-insulating conditions in the samples, which would result in a mid band gap Fermi level position, the Ga vacancies would be in a triple negative charge state and then have no magnetic moment. We then decided to look for alternative defects that would have similar characteristics of the Ga vacancy of producing a magnetic moment. Following the idea that they should have N dangling bonds or non-bonding states, we tried nitrogen interstitials next to a Gd in the octahedral interstitial site. We

also tried O interstitials starting from the idea that oxygen might migrate close to Gd. These ideas were based on the notion that Gd actually prefers octahedral bonding as is clear from both GdN and Gd_2O_3. We found that both interstitial N and O next to Gd gave magnetic moments and provided ferromagnetic interactions between Gd atoms. We then further pursued this model by studying the distance dependence of the interactions between Gd spins and N interstitial spins. Finally, we also examined the energetics and found that both N and O interstitials are attracted toward the Gd because they have a lower energy when situated next to a Gd atom. We also found support for the interstitial idea in the already published literature. The results of this investigation were published in PRB as a Rapid Communication.[25]

Our most important result of the project is thus that N interstitials and possibly O interstitials are likely candidates in causing the ferromagnetism in Gd doped GaN. While not explaining the colossal magnetic moments, they do lead to additional sources of magnetic moment besides the Gd 4f electrons. They couple ferromagnetic between each other and Gd and cause the Gd 4f moments to align themselves with the N moments and with each other. These interactions are sufficiently long range and strong to at least in a qualitative sense explain ferromagnetism up to elevated temperatures. They maintain their magnetic moments even with the Fermi level pinned at mid gap positions and consistent with the known semi-insulating nature of most magnetic Gd doped GaN samples. We found it was favorable for substitutional O to move toward a near Gd octahedral interstitial site, as long as it the chemical potential of N is high enough (as occurs in a growth environment) so as to readily fill the resulting N vacancy. We also found that N interstitials are attracted toward Gd. N interstitials are furthermore found to be relatively low energy of formation native defects. After N vacancies they are the next easy to form defect for mid-gap Fermi level positions. One can also easily imagine that nitrogen vacancy-interstitial pairs form abundantly during Gd implantation.

While further work will be necessary to fully explore this model, it is at present the most plausible model to explain ferromagnetic behavior. In reality the situation may be more complex however, because phase separation issues and clustering of Gd also appear to occur in real samples.[17, 18, 16] It is not possible at this moment however to explain colossal magnetic moments, and this claim thus remains doubtful in our opinion.

During the no-cost extension period of the grant, we studied the recent proposal by Ney et al. [26] that Gd occurs in part on N sites as well as on Ga sites. Furthermore these authors proposed that the XLD spectra

measured by them could only be simulated properly by including pairs of adjacent Gd on Ga and N sites. We thus performed calculations to determine the site preference of Gd on N and Ga sites and for the adjacent pair and investigated how this affects the electronic stucture and magnetism. We found, as expected, that Gd on N sites is a high energy formation defect of order 14 eV/Gd even in optimal conditions, of N poor, Gd rich chemical potentials. The system significantly relaxes with outward relaxation of the atoms around the Gd on N site. Even when we allowed the volume of the cell to relax the energy stayed high. For the pair, we find also a strong relaxation, in which the Gd atoms repel each other such that the Gd moves away from the N site toward an intersitital site. This situation has lower energy that the isolated Gd_{Ga}, Gd_N but stil high energy. The electronic structure of Gd on N is more perturbed leading to a defect level in the gap. Nonetheless after full relaxation, the magnetic moments just add up to those of the individual Gd atoms, meaning that the two stayed ferromagnetically coupled. In view of the large energy of formation, the occurence of Gd on N sites and in paris close to Gd_{Ga} appears unlikely in thermodynamic equilibrium and should thus not affect the major magnetic properties of the samples. The partial densities of states were calculated and the relation to the XLD spectra will be investigated. This work will be presented at the MRS Fall-Meeting Symposium I, on which more later.

From July 2010-September 2010, our group hosts a German exchange graduate student, Alexander Thiess, from Stephan Blügel's group at the Institute for Solid State Research in Jülich. He is applying the Korringa-Kohn-Rostoker multiple scattering approach, with a program specially designed for the study of very large systems. We are using this approach to investigate the magnetic exchange coupling between Gd atoms and N interstitials as function of distance. It is too early to evalaute the final results of this approach but initial findings seem to confirm the results of our earlier study.[25]

During the project, additional work was initiated on related subjects. For example, in order to fully understand and model ferromagnetic Curie temperatures, we realized that a systematic study of the exchange interactions would be necessary. To this end, we studied the linear response approach of Liechtenstein et al. [27] Our previous work on another dilute magnetic semiconductor system, Mn-doped ScN was finalized during the present project using this approach. We also performed significant work to apply this method to Gd in GdN.

We also decided that a more thorough understanding of magnetism in bulk GdN and related rare-earth nitrides would be of interest to the project

and possibly useful for understanding the properties of rare-earth doped GaN. During the course of the project, we became funded by NSF to study rare-earth nitrides through a Materials World Network proposal. Our work on bulk rare-earth nitrides at that point was shifted to the NSF project but a few initial studies were partially funded by the present ARO grant and acknowledged in publications.[28, 29]

Our work on magnetism in GdN led to the idea that it is primarily the Gd-d states that are responsible for the magnetic exchange interactions. Even though in GdN these states are nominally empty, small magnetic moments are induced in Gd-d states and N p-states and they were found to be primarily responsible for the exchange interactions while the much larger f magnetic moments are residing in orbitals that are too localized to exhibit any sizable interatomic interactions. The intra-atomic interactions however lock them into place with the Gd-d states and it was found that an antiferromagnetic arrangement of Gd-d and N$-p$ small moments corresponds to a ferromagnetic Gd moment alignment. These results were published under NSF funding in [30] but are nevertheless of relevance to the present project. In fact, we found that even in bulk GdN, our model leads to much lower Curie temperatures than observed experimentally, even though the same model quantitatively explains the Néel temperatures in GdP, GdAs, GdSb and GdBi and the Curie temperature in bulk Gd. Possibly defect induced magnetism, for example caused by N vacancies may play a crucial role even in bulk GdN. Very recently, under the NSF grant we studied the effect of N-vacancies on the electronic structure and magnetism of GdN.

Some other nitride semiconductors besides GaN are possibly useful as dilute magnetic semiconductor hosts: Zn-IV-N_2 semiconductors had been studied by us in the context of an AFOSR proposal which however, terminated before we could finish the work. In view of their possible future uses for magnetic semiconductors, we continued some work on these materials with partial support from ARO and acknowledged ARO's contributions in the related publications.[31, 32] Finally, we also performed some work on AlN/GaN superlattice phonons and infrared spectra which was recently submitted to PRB.[33]

Finally, we mention the results of the project in terms of human resources formation and other broader impacts. One graduate student, Chandrima Mitra successfully completed here Ph.D. thesis and since moved on to a postdoctoral position at a Max-Planck research institute in Germany. Two additional students worked on the project during the last year under the no-cost extension: Atchara Punya and Tawinan Cheiwchanchamnangij.

As part of our efforts to disseminate our work, we successfully proposed

and are currently organizing a Symposium at the MRS Fall Meeting 2010. The symposium is entitled: "Magnetism and Correlated Electronic Structure of Nitrides; Rare-Earth and Transition Metals as Constituents and Dopants." This symposium will bring together researchers in the field of Rare-earth doped GaN with researchers in the field of bulk rare-earth nitrides. It is also broadened by including transition metal bulk nitrides and transition metal doped GaN magnetic semiconductors.

4 Outlook for Future Work

We end with an outlook toward future work. First of all, some additional work is already underway to study intersititals in wurtzite GaN, including the so-called split interstitial configuration. Secondly, we plan to use the linear response approach to study the exchange interactions due to N interstitials and Gd more systematically. The latter approach was found to be very powerfull to explore the full dependence of exchange interactions on doping, distance, random nature of alloys. Recent investigations of Gd doped GaN indicate the possibility of at least partial phase separation. We thus plan to investigate the role of either small Gd or GdN clusters in GaN. In addition, our results on intersitital oxygen indicate that studies of Gd_2O_3 might be wortwhile. We also plan to study models of Gd with more than one interestitials as its neighbors to find out at what point there is a transition to local octahedral bonding. To move toward the study of other rare-earth ions, we believe it will be necessary to include the multiplet splittings of the f electrons into the band structure framework. This can be done in the framework of dynamic mean field theory and we are starting to do preparatory work in that direction. This was the main topic of a renewal proposal sumbitted earlier in 2010 and currently pending with ARO.

References

[1] N. Teraguchi, A. Suzuki, Y. Nanishi, Y.-K. Zhou, M. Hashimoto, and H. Asahi, "Room-temperature observation of ferromagnetism in diluted magnetic semiconductor GaGdN grown by RF-molecular beam epitaxy," *Solid State Commun.*, vol. 122, no. 12, pp. 651 – 653, 2002.

[2] H. Asahi, Y. K. Zhou, M. Hashimoto, M. S. Kim, X. J. Li, S. Emura, and S. Hasegawa, "GaN-based magnetic semiconductors for nanospin-

tronics," *Journal of Physics: Condensed Matter*, vol. 16, no. 48, pp. S5555–S5562, 2004.

[3] S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, "Colossal Magnetic Moment of Gd in GaN," *Phys. Rev. Lett.*, vol. 94, p. 037205, Jan 2005.

[4] S. Dhar, L. Pérez, O. Brandt, A. Trampert, K. H. Ploog, J. Keller, and B. Beschoten, "Gd-doped GaN: A very dilute ferromagnetic semiconductor with a Curie temperature above 300 K," *Phys. Rev. B*, vol. 72, p. 245203, Dec 2005.

[5] S. Dhar, T. Kammermeier, A. Ney, L. Pérez, K. H. Ploog, A. Melnikov, and A. D. Wieck, "Ferromagnetism and colossal magnetic moment in Gd-focused ion-beam-implanted GaN," *Appl. Phys. Lett.*, vol. 89, no. 6, p. 062503, 2006.

[6] M. A. Khaderbad, S. Dhar, L. Pérez, K. H. Ploog, A. Melnikov, and A. D. Wieck, "Effect of annealing on the magnetic properties of Gd focused ion beam implanted GaN," *Appl. Phys. Lett.*, vol. 91, no. 7, p. 072514, 2007.

[7] J. Hite, R. Frazier, R. Davies, G. Thaler, C. Abernathy, S. Pearton, E. Brown, and U. Hmmerich, "GaN-based magnetic semiconductors for nanospintronics," *Journal of Electronic Materials*, vol. 36, no. 4, 2007.

[8] J. K. Hite, K. K. Allums, G. T. Thaler, C. R. Abernathy, S. J. Pearton, R. M. Frazier, R. Dwivedi, R. Wilkins, and J. M. Zavada, "Effects of proton irradiation on the magnetic properties of GaGdN and GaCrN," *New Journal of Physics*, vol. 10, no. 5, p. 055005 (8pp), 2008.

[9] J. M. Zavada, N. Nepal, J. Y. Lin, H. X. Jiang, E. Brown, U. Hömmerich, J. Hite, G. T. Thaler, C. R. Abernathy, S. J. Pearton, and R. Gwilliam, "Ultraviolet photoluminescence from Gd-implanted AlN epilayers," *Appl. Phys. Lett.*, vol. 89, no. 15, p. 152107, 2006.

[10] J. Hite, G. T. Thaler, R. Khanna, C. R. Abernathy, S. J. Pearton, J. H. Park, A. J. Steckl, and J. M. Zavada, "Optical and magnetic properties of Eu-doped GaN," *Appl. Phys. Lett.*, vol. 89, no. 13, p. 132119, 2006.

[11] N. Nepal, S. M. Bedair, N. A. El-Masry, D. S. Lee, A. J. Steckl, and J. M. Zavada, "Correlation between compositional fluctuation and mag-

netic properties of Tm-doped AlGaN alloys," *Appl. Phys. Lett.*, vol. 91, no. 22, p. 222503, 2007.

[12] J. M. Zavada, N. Nepal, C. Ugolini, J. Y. Lin, H. X. Jiang, R. Davies, J. Hite, C. R. Abernathy, S. J. Pearton, E. E. Brown, and U. Hömmerich, "Optical and magnetic behavior of erbium-doped GaN epilayers grown by metal-organic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 91, no. 5, p. 054106, 2007.

[13] N. Nepal, J. M. Zavada, R. Dahal, C. Ugolini, A. Sedhain, J. Y. Lin, and H. X. Jiang, "Optical enhancement of room temperature ferromagnetism in Er-doped GaN epilayers," *Appl. Phys. Lett.*, vol. 95, no. 2, p. 022510, 2009.

[14] S. Y. Han, J. Hite, G. T. Thaler, R. M. Frazier, C. R. Abernathy, S. J. Pearton, H. K. Choi, W. O. Lee, Y. D. Park, J. M. Zavada, and R. Gwilliam, "Effect of Gd implantation on the structural and magnetic properties of GaN and AlN," *Appl. Phys. Lett.*, vol. 88, no. 4, p. 042102, 2006.

[15] J. Hejtmánek, K. Knížek, M. Maryško, Z. Jirák, D. Sedmidubský, Z. Sofer, V. Peřina, H. Hardtdegen, and C. Buchal, "On the magnetic properties of Gd implanted GaN," *Proceedings of the 52nd Annual Conference on Magnetism and Magnetic Materials*, vol. 103, no. 7, p. 07D107, 2008.

[16] T. Kammermeier, S. Dhar, V. Ney, E. Manuel, A. Ney, K. H. Ploog, F.-Y. Lo, A. Melnikov, and A. D. Wieck, "Paramagnetic and ferromagnetic resonance studies on dilute magnetic semiconductors based on GaN," *Phys. Stat. Solidi (a)*, vol. 205, pp. 1872–1875, 2008.

[17] A. Ney, T. Kammermeier, E. Manuel, V. Ney, S. Dhar, K. H. Ploog, F. Wilhelm, and A. Rogalev, "Element specific investigations of the structural and magnetic properties of Gd:GaN," *Appl. Phys. Lett.*, vol. 90, no. 25, p. 252515, 2007.

[18] A. Ney, T. Kammermeier, V. Ney, S. Ye, K. Ollefs, E. Manuel, S. Dhar, K. H. Ploog, E. Arenholz, F. Wilhelm, and A. Rogalev, "Element specific magnetic properties of Gd-doped GaN: Very small polarization of Ga and paramagnetism of Gd," *Phys. Rev. B*, vol. 77, no. 23, p. 233308, 2008.

[19] G. M. Dalpian and S.-H. Wei, "Electron-induced stabilization of ferromagnetism in $Ga1 - xGdxN$," *Phys. Rev. B*, vol. 72, p. 115201, Sep 2005.

[20] W. R. L. Lambrecht and P. Larson, "Gadolinium and Oxygen co-doping of Gallium Nitride: an LSDA + U study," in *Advances in III-V Nitride Semiconductor Materials and Devices* (C. R. Abernathy, H. Jiang, and J. M. Zavada, eds.), vol. 955E, pp. 0955–I01–05, Mater. Res. Soc. Symp. Proc., 2006.

[21] L. Liu, P. Y. Yu, Z. Ma, and S. S. Mao, "Ferromagnetism in GaN:Gd: A Density Functional Theory Study," *Phys. Rev. Lett.*, vol. 100, no. 12, p. 127203, 2008.

[22] P. Dev, Y. Xue, and P. Zhang, "Defect-Induced Intrinsic Magnetism in Wide-Gap III Nitrides," *Phys. Rev. Lett.*, vol. 100, no. 11, p. 117204, 2008.

[23] Y. Gohda and A. Oshiyama, "Intrinsic ferromagnetism due to cation vacancies in Gd-doped GaN: First-principles calculations," *Phys. Rev. B*, vol. 78, no. 16, p. 161201(R), 2008.

[24] C. Mitra, *Computational studies of Gadolinium in Nitrides: bulk GdN and Gd-doped GaN*. PhD thesis, Case Western Reserve University, 2009.

[25] C. Mitra and W. R. L. Lambrecht, "Interstitial-nitrogen- and oxygen-induced magnetism in Gd-doped GaN," *Phys. Rev. B*, vol. 80, p. 081202, Aug 2009.

[26] A. Ney, T. Kammermeier, K. Ollefs, V. Ney, S. Ye, S. Dhar, K. H. Ploog, M. Röver, J. Malindretos, A. Rizzi, F. Wilhelm, and A. Rogalev, "Gd-doped GaN studied with element specificity: Very small polarization of Ga, paramagnetism of Gd and the formation of magnetic clusters," *J. Mag. Magn. Mater.*, vol. 322, pp. 1162–1166, 2010.

[27] A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, "Local spin density functional approach to the theory of exchange interactions in ferromagnetic metals and alloys," *J. Magn. Magn. Mater.*, vol. 67, pp. 65–74, 1987.

[28] H. J. Trodahl, A. R. H. Preston, J. Zhong, B. J. Ruck, N. M. Strickland, C. Mitra, and W. R. L. Lambrecht, "Ferromagnetic redshift of the optical gap in GdN," *Phys. Rev. B*, vol. 76, no. 8, p. 085211, 2007.

[29] A. R. H. Preston, S. Granville, D. H. Housden, B. Ludbrook, B. J. Ruck, H. J. Trodahl, A. Bittar, G. V. M. Williams, J. E. Downes, A. DeMasi, Y. Zhang, K. E. Smith, and W. R. L. Lambrecht, "Comparison between experiment and calculated band structures for DyN and SmN," *Phys. Rev. B*, vol. 76, no. 24, p. 245120, 2007.

[30] C. Mitra and W. R. L. Lambrecht, "Magnetic exchange interactions in the gadolinium pnictides from first principles," *Physical Review B (Condensed Matter and Materials Physics)*, vol. 78, no. 13, p. 134421, 2008.

[31] T. J. Peshek, T. R. Paudel, K. Kash, and W. R. L. Lambrecht, "Vibrational modes in ZnGeN[sub 2]: Raman study and theory," *Phys. Rev. B*, vol. 77, no. 23, p. 235213, 2008.

[32] T. R. Paudel and W. R. L. Lambrecht, "First-principles calculations of elasticity, polarization-related properties, and nonlinear optical coefficients in Zn-IV-N[sub 2] compounds," *Phys. Rev. B*, vol. 79, no. 24, p. 245205, 2009.

[33] T. R. Paudel and W. R. L. Lambrecht, "Computational study of phonon modes in short-period AlN/GaN superlattices," *Phys. Rev. B*, vol. 80, p. 104202, Sep 2009.